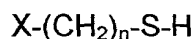


embodiments include, without limitation, a spin coating method, a dip coating method, and a spray coating method. A spin coating method is preferred, and is described in U.S. Patent No. 6,001,418 to DeSimone et al., the disclosure of which is incorporated herein by reference in its entirety. A meniscus

5 coating technique can also be employed such as one described, for example, in U.S. Patent No. 6,083,565 to Carbonell et al., the disclosure of which is incorporated herein by reference in its entirety. A coating method using self-assembling monolayers (SAMs) can also be employed, and may be used in conjunction with CO₂. Examples of molecules that are capable of producing
10 SAMs include, without limitation, alkane thiols, fluorinated alkane thiols, and functionalized alkane thiols such as those represented by the formula:



wherein X may be -CN, -COOH, -OCH₃, -(OCH₂CH₂)_n-OH, -(OCH₂CH₂)_n-OCH₃, -H, phenyl, or substituted phenyl, and n ranges from 1 to 1,000, and
15 more preferably from 2 to 20.

A wide range of components can be used in the present invention to form a coating on the substrate. For the purposes of the invention, the term "materials" can include, without limitation, precursors, monomers, polymeric materials, and the like. Polymers, polymeric precursors, and monomers that
20 are soluble or insoluble in CO₂ or CO₂ mixed with other gases (insert or otherwise) and co-solvents including surfactants may be necessary to maintain low surface tension and solubility and viscosity as CO₂ evaporates, at a number of density and/or pressure conditions are encompassed by the invention. Examples of suitable embodiments include polymeric materials
25 which comprise, without limitation, fluoropolymers, silicon-containing polymers, or combinations thereof, such polymers having a CO₂-soluble or "CO₂-philic" component. "CO₂-philic" refers to the polymer having an affinity for carbon dioxide. Examples of suitable monomers for making the fluoropolymers are numerous and include, but are not limited to, those set
30 forth in U.S. Patent No. 5,739,223 to DeSimone et al., the disclosure of which is incorporated herein by reference in its entirety. Carbon dioxide soluble monomers may be employed if so desired. Exemplary monomers are

fluoroacrylate monomers, fluorostyrene monomers, fluoroalkylene oxide monomers, fluorolefin monomers, fluorinated alkyl vinyl ether monomers, cyclic fluorinated monomers, and mixtures thereof. Specific preferred monomers include, without limitation, 2-(N-ethylperfluorooctane- sulfonamido) ethyl acrylate, 2-(N-ethylperfluorooctane- sulfonamido) ethyl methacrylate, 2-(N-methylperfluorooctane- sulfonamido) ethyl acrylate, 2-(N-methylperfluorooctane- sulfonamido) ethyl methacrylate, 1,1'-dihydroparfluorooctyl acrylate, 1,1'-dihydroparfluorooctyl methacrylate, 1,1',2,2'-tetrahydroparfluoroalkylacrylate, 1,1',2,2'-tetrahydroparfluoroalkyl methacrylate, α -fluorostyrene, 2,4,6-trifluoromethylstyrene, hexafluoropropylene oxide, perfluorocyclohexane oxide, tetrafluoroethylene, vinylidene fluoride, chlorotrifluoroethylene, perfluoro(propyl vinyl ether), perfluoro(methyl vinyl ether), 2,2-bis-trifluoromethyl-4,5-difluoro-1,3-dioxole, and mixtures thereof, including those set forth in U.S. Patent No. 6,083,565 to Carbonell et al., the disclosure of which is incorporated herein in its entirety by reference.

Any number of silicon-containing polymers can be used in the present invention, the selection of which is known by those skilled in the art. Examples of silicon-containing polymers include those containing at least one segment such as, without limitation, an alkyl siloxane, a fluoroalkyl siloxane, a chloroalkyl siloxane, and mixtures thereof.

Various polymeric materials that may be used in forming the coating (e.g., photoresist resin) include, without limitation, a polymer resin formed from a t-butyl norbornyl group, maleic anhydride, a fluorinated norbornyl group, and acrylic acid. Such a resin is particularly effective at a radiation of 193 nm wavelength. Another example of a suitable resin is an O₂-RIE (Reactive Ion Etch) resistant random terpolymer of 1,1'-dihydroparfluorooctyl methacrylate ("FOMA"), t-butyl methacrylate ("TBM"), and a poly(dimethylsiloxane) macromonomer such as, for example,

$$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{CH}_2-(\text{Si}(\text{CH}_3)_2\text{O})_n-\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$

wherein n ranges from 1 to 10,000.

Monomers that may be used include, without limitation, carbon dioxide soluble monomers such as those fluoro- and silicon monomers described herein, as well as (meth)acrylate monomers (e.g., methyl (meth)acrylate) and aryl vinyl monomers (e.g., styrene). These monomers, as well as polymeric
5 precursors, may be deposited as a thin film on the substrate, and polymerized thereon using any suitable technique such as, for example, thermal or photo-chemical means, including those described in U.S. Patent No. 6,083,565 to Carbonell et al.,.

As described above, the coating is imagewise exposed to radiation as
10 described in U.S. Patent No. 5,665,527 to Allen et al., the disclosure of which is incorporated herein by reference in its entirety. Various radiation techniques including electromagnetic radiation such as deep ultraviolet or X-ray, more preferably deep ultraviolet radiation suitably at a wavelength of about 150-250 nm (248/254 nm), preferably 157 and 193 nm, and e-beam.
15 Suitable radiation sources include, without limitation, mercury, mercury/xenon, xenon lamps, and X-ray. Visible radiation can also be employed. A typical radiation source is ArF excimer or KrF excimer.

The invention may optionally include other embodiments. In one aspect for example, the invention may further comprise the steps of
20 depositing a metal-containing material or an ionic material on the surface of the substrate from which the exposed or the unexposed coating portions was removed, and removing the remaining (exposed or unexposed) coating portion from the substrate. The step of depositing a metal-containing material or an ionic material can be carried out (e.g., processed) by any number of
25 methods including, without limitation, ion implant, metal deposition, and the like. Metal depositions techniques include, without limitation, evaporation sputtering, chemical vapor deposition, or laser-induced deposition. Suitable metal-containing materials include conductive metals such as, but not limited to, aluminum, copper, gold, titanium, tantalum, tungsten, molybdenum, silver,
30 combinations thereof, and alloys thereof. Suitable ionic materials include, but are not limited to, inorganic ions such as boron, phosphorous, or arsenic which can be implanted. Accordingly, n- or p-doped transistors can be